



High-voltage performance of LiCoO₂/graphite batteries with methylene methanedisulfonate as electrolyte additive

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H I G H L I G H T S

- ▶ MMDS is newly evaluated as an electrolyte additive.
- ▶ This additive tends to be decomposed on LiCoO₂ cathode prior to the solvents.
- ▶ A highly ionic conductivity film can be formed using MMDS in the electrolyte.
- ▶ The cycle performance of LIB (3.0–4.5 V) can be improved using this additive.

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In order to overcome the capacity fading of LiCoO₂/graphite Lithium-ion batteries (LIBs) cycled in the voltage range of 3.0–4.5 V (vs. Li/Li⁺), methylene methanedisulfonate (MMDS) is newly evaluated as an electrolyte additive. The linear sweep voltammetry (LSV) and cyclic voltammetry (CV) indicate that MMDS has a lower oxidation potential in the mixed solvents of ethylene carbonate (EC) and ethyl methyl carbonate (EMC), and participates in the formation process of the cathode electrolyte interface (CEI) film. With the addition of 0.5 wt.% MMDS into the electrolyte, the capacity retention of the LiCoO₂/graphite cells cycled in 3.0–4.5 V is significantly increased from 32.0% to 69.6% after 150 cycles, and the rate capacity is also improved compared with the cells without MMDS additive in the electrolyte, showing the promising prospect in the electrolyte. In addition, the results of electrochemical impedance spectroscopy (EIS), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) demonstrate that the enhanced electrochemical performances of the cells can be ascribed to the modification of components of cathodes surface layer in the presence of MMDS, which resulting the suppression of the electrolyte oxidized decomposition and the improvement of CEI conductivity.

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1. Introduction

Application of lithium-ion batteries (LIBs) has extended to portable electronic devices and energy storage since LIBs have many advantages such as higher work voltage, superior energy density and environmental friendly compared to other secondary batteries [1,2]. To meet the higher capacity and longer cycle life requirements of LIBs for electrical vehicles and new electronic devices, many researches are being focused on the development of the cathodes with higher working potentials [3–6]. LiCoO₂, as the most successful commercial cathode material, has been widely used in the LIBs due to its virtues such as easy preparation,

structural stability and long cycle life. Charging the LiCoO₂ above 4.2 V is proposed to be an effective way to increase its reversible capacity. However, overcharging LiCoO₂ can catalyze the oxidation of the electrolyte at higher potentials, leave a highly resistive surface film on the cathode, and correspondingly lead to the capacity fade in the following cycles [7–9].

The surface modification of LiCoO₂ with metal oxides such as Al₂O₃, SiO₂, MgO, AlPO₄ and ZnO has been tried to improve its cycle performance at higher voltage [10–12]. However, these metal oxides can not form a uniform surface protective film on the LiCoO₂ active material, which tends to act as an inert layer to ionic conduction, and also requires complex and high-cost procedures. These limitations motivate people to demonstrate a more easy and effective method through adding functional additives into the electrolyte. Abe et al. [13] investigated several organic additives, i.e. biphenyl(BP), o-terphenyl (OTP), furan and so on, which tend to be

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electrochemically polymerized in the high potential region, and form a conductive film on the LiCoO_2 cathode. Lee et al. [14] reported the performances of LIBs with LiCoO_2 at a cutoff voltage of 4.4 V using N -(triphenylphosphoranylidene) aniline (TPPA) as electrolyte additive. The results showed that TPPA could modify the surface films of LiCoO_2 electrodes, and then suppress the decomposition of both the solvent and salt in electrolyte. However, such proposed additives, with benzene group in their structures, maybe have some negative effects to LIBs in charge-discharge cycles.

Herein, we present an investigation of a new electrolyte additive, Methylene methanedisulfonate (MMDS, its structure is shown in Fig. 1), in $1 \text{ mol L}^{-1} \text{ LiPF}_6$ in the mixed solvents of ethylene carbonate (EC) and ethyl methyl carbonate (EMC, EC:EMC = 1:2, wt.%) using LiCoO_2 as cathode material. The electrochemical behavior of MMDS and its effect on the performances of LiCoO_2 electrode at high voltage operation were studied via combination of linear sweep voltammetry (LSV), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and battery performance test, X-ray photoelectron spectroscopy (XPS), as well as transmission electron microscopy (TEM).

2. Experimental

2.1. Preparation of electrolyte and electrode

Battery-grade carbonates solvents and lithium hexa-fluorophosphate (LiPF_6) were obtained from Guangzhou Tinci Materials Technology Co., Ltd. Methylene methanedisulfonate (MMDS, 99.7%) was purchased from Aldrich, they were all used without further purification. The composition of the electrolyte used in all of the cells was $1 \text{ mol L}^{-1} \text{ LiPF}_6$ -EC:EMC (1:2, wt.%). Considering the solubility of MMDS, the ionic conductivity of electrolyte, and the effects of MMDS on the electrochemical performances of battery, the content of MMDS added in the electrolyte was ultimately determined to be 0.5 wt.%. The water and free acid (HF) contents in the electrolyte were controlled to be less than 20 ppm and 50 ppm, respectively, determined by auto moisture titration instrument (KF 831 Metrohm, Swiss) and automatic potentiometric titrator (798 Metrohm, Swiss). The cathode electrodes were prepared by combining 94.0 wt.% LiCoO_2 (Hunan Reshine New Material Co., Ltd), 3.0 wt.% conductive carbon, and 3.0 wt.% polyvinylidene fluoride (PVDF). Anode electrodes contained 95.0 wt.% graphite (BTR Battery Materials Co., Ltd), 1.0 wt.% Super-P, 1.5 wt.% carboxymethyl cellulose (CMC) and 2.5 wt.% styrene butadiene rubber (SBR). Both electrodes were dried at 120°C for 10 h under vacuum condition prior to the assembling operation.

2.2. Measurements

The electrochemical window of the electrolyte was examined by linear sweep voltammetry (LSV) using an Instrumental

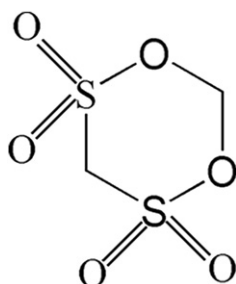


Fig. 1. The molecule structure of MMDS.

Electrochemical Workstation (CHI660, Chenhua, Shanghai) on a Pt working electrode with lithium as both counter and reference electrodes. The Pt electrode was made directly by sealing a Pt wire (100 μm diameter) in a glass tube. CHI660 was also used to carry out the cyclic voltammetry (CV) measurements in a three-electrode cell, with LiCoO_2 as the working electrode and lithium foil as both counter and reference electrode.

Pouch cells with and without MMDS in the electrolyte were fabricated to evaluate the real effects of MMDS on the electrochemical performances of LIBs at high charge cut-off voltage. Their charge-discharge performances were tested by using a computer-controlled battery charger test (BS-9300R, Qingtian, Guangzhou). The cells were firstly charged to 4.2 V at a constant current of 1 C rate, followed by a constant potential of 4.2 V until the current reached C/20, and then discharged to 3.0 V at a constant current of 1C rate. To evaluate high voltage performance of LiCoO_2 , the cells were charged to 4.5 V at a constant current of 1C rate, followed by a constant potential of 4.5 V until the current reached C/20, and then discharged to 3.0 V at a constant current of 1 C rate. The electrochemical impedance spectroscopy (EIS) of the cells charged to 4.5 V after one cycle and 150 cycles were measured with frequency response analyzer (FRA, Solartron 1455A, England). Frequency of impedance ranges from 100 kHz to 0.01 Hz at an amplitude of 10 mV.

The chemical composition of the surface layer on the LiCoO_2 was analyzed by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos) with Al K α line as an X-ray source. After 150 cycles at room temperature, the LiCoO_2 cathode was carefully separated from the cell and subsequently rinsed with a dimethyl carbonate (DMC) solvent to remove the residual electrolyte, and then dried under

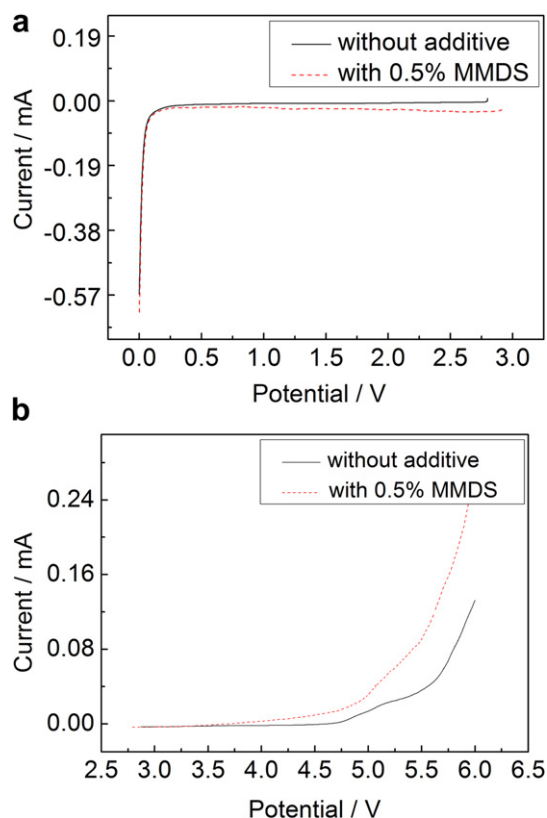


Fig. 2. The electrochemical window of electrolyte using linear sweep voltammetry at Pt electrode in $1 \text{ mol L}^{-1} \text{ LiPF}_6$ -EC:EMC (1:2, wt.%) with and without 0.5 wt.% MMDS at 1.0 mV s^{-1} (a): OCV-0.0 V; (b): OCV-6.0 V.

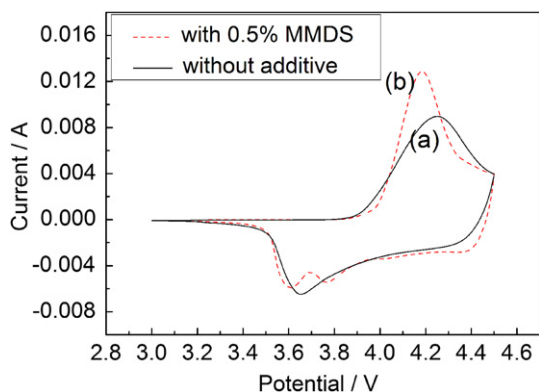


Fig. 3. Cyclic voltammetry of LiCoO_2 in $1 \text{ mol L}^{-1} \text{LiPF}_6\text{-EC:EMC (1:2, wt.\%)}$ (a) without and (b) With 0.5 wt.% MMDS additive at 0.1 mV s^{-1} .

vacuum at room temperature prior to being packed into a sealed aluminum plastic bag before XPS analysis. Transmission electron microscopy (TEM, JEM-2100, JOEL, Japan) was used to characterize the surface morphology of the LiCoO_2 cathode.

3. Results and discussion

3.1. Evaluation of the possibility of MMDS as the cathode additives

The electrochemical windows of the electrolytes with and without MMDS additive were comparatively measured by LSV at Pt electrode with three-electrode cell. As shown in Fig. 2(a), no distinct reduction peaks can be observed compared to the electrolyte without MMDS additive, which implies a good stability or compatibility of the electrolyte containing MMDS with anode of LIB. From Fig. 2(b), the reference electrolyte without additive is decomposed at 5.3 V, while the electrolyte with 0.5 wt.% MMDS is oxidized at 5.1 V as indicated by the sharp current increase. As expected, MMDS has lower oxidation potential than those of the solvents, which indicates the additive is likely to be decomposed on LiCoO_2 cathode prior to the solvents, and may result in the suppression of the electrolyte oxidized decomposition.

In order to further investigate the effect of MMDS on the LiCoO_2 cathode, the CVs of LiCoO_2 cathode was measured. As seen in Fig. 3(a), an oxidation peak at 4.2 V and a reduction peak at 3.7 V can be observed, which are related to Li^+ extraction and insertion, respectively. For the electrolyte with MMDS, a higher current peak

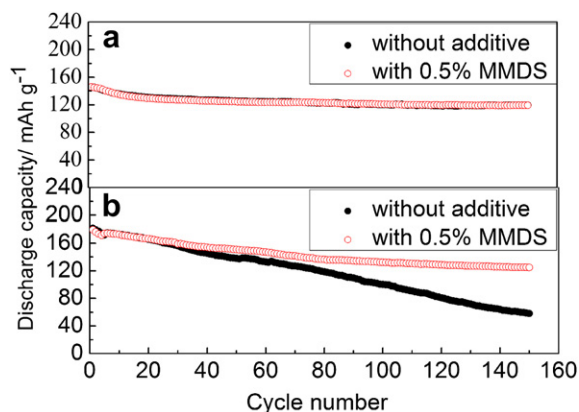


Fig. 4. Discharge capacity of cells as a function of cycle number obtained at different cut-off potentials: (a) 3.0–4.2 V, (b) 3.0–4.5 V.

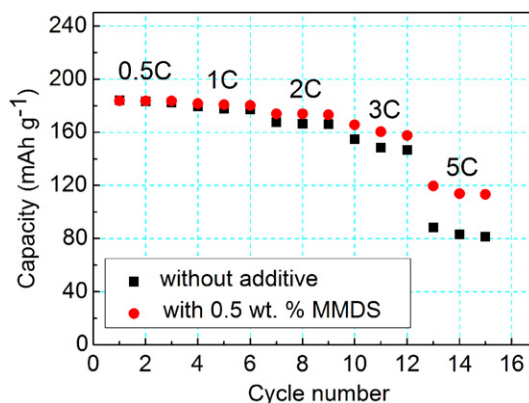


Fig. 5. Rate performances of the $\text{LiCoO}_2/\text{graphite}$ cells with and without MMDS in the electrolyte.

near 4.2 V can be seen from Fig. 3(b) when the potential is swept from the open circuit voltage (OCV) to 4.5 V. The oxidation potential of MMDS on LiCoO_2 cathode is almost equal to the Li^+ extraction potential, the two peaks are nearly overlapped, and thus enhance the intensity of current peak at 4.2 V. During the reverse sweeping from 4.5 V to 3.0 V, two reduction peaks are observed. The reduction current peaks at 3.6 V and 3.8 V are ascribed to the Li^+ insertion to LiCoO_2 and the reduction of decomposed products of MMDS on LiCoO_2 cathode, respectively. The CV results indicate that MMDS is supposed to participate the formation process of the CEI film on the LiCoO_2 cathode.

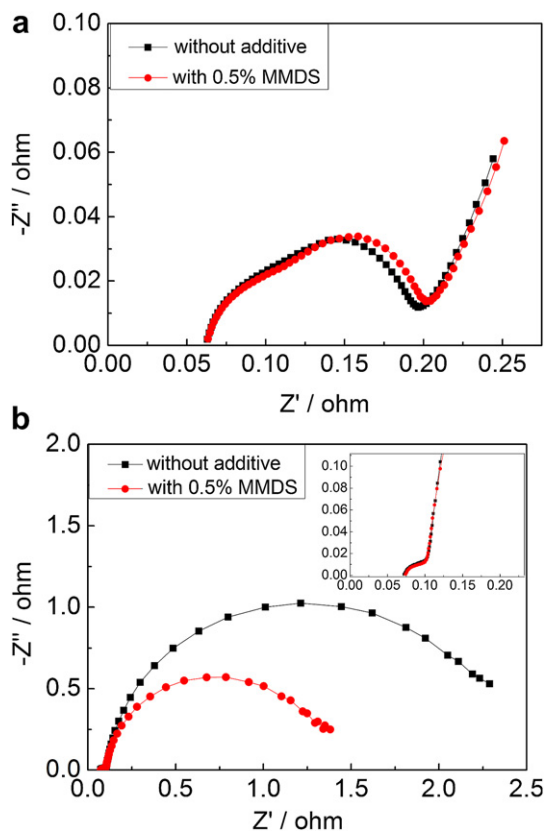


Fig. 6. Electrochemical impedance spectra of $\text{LiCoO}_2/\text{graphite}$ cells with and without MMDS charged to 4.5 V after one cycle (a) and 150 cycles (b).

Table 1

Element concentrations on the surface layer of the LiCoO₂ electrodes cycled in 1 mol L⁻¹ LiPF₆ in EC:EMC(1:2) without and with 0.5% MMDS by XPS.

Elements	C 1s	O 1s	F 1s	Co 2p	P 2p	S 2p
Without additive	54.22	18.98	24.06	1.77	0.97	—
With additive	52.11	20.93	21.88	1.30	1.01	2.77

3.2. Electrochemical properties of MMDS in LIBs

The effects of MMDS additive on the cycle performance of LIBs charged to 4.2 V and 4.5 V were evaluated, as shown in Fig. 4(a) and Fig. 4(b). It can be seen that about 25% additional capacity is realized by extending the charge potential beyond the traditional 4.2 V limit to 4.5 V. As presented in Fig. 4(a), the cells charged to 4.2 V show similar cycling performance irrespective of the introduction of MMDS. The results confirm that the addition of MMDS does not affect the performance of the cells cycled in the voltage of 3.0–4.2 V. Whereas, the cell with MMDS in the electrolyte exhibits a significantly improved cycle performance when the cells are charged to 4.5 V as shown in Fig. 4(b). The initial discharge capacities of both cells are almost identical. As the numbers of cycle increases, the discharge capacity of the cell without additive is gradually fading [58.0 mAh g⁻¹ after 150 cycles, 32.0% of the initial discharge capacity (181.5 mAh g⁻¹)], while the cell with MMDS additive in the electrolyte enhanced the performance up to 69.6% (124.9 mAh g⁻¹) of its initial discharge capacity (179.5 mAh g⁻¹). It is obvious that the addition of MMDS into the electrolyte improves the cyclic stability of LIBs at high voltage.

Fig. 5 presents the rate capacities of the cells with and without MMDS in the electrolyte. The cell with MMDS in the electrolyte has higher discharge capacity than that of without additive in the electrolyte, especially when the discharge rate is 5C. The cell using MMDS in the electrolyte provides approximately 115.6 mAh g⁻¹ of the discharge capacity at 5C, while the cell without additive in the electrolyte keeps only 84.3 mAh g⁻¹, indicating that the migration of Li⁺ is prompted by the surface film derived from MMDS, and hence enhances the rate performance of lithium ion cell.

Fig. 6 shows the impedance measurement results of the cells after one cycle and 150 cycles. The high-frequency semicircle is attributed to the solid electrolyte interface resistance which likely occurs at both anode and cathode, and the semicircle at mid-frequency is typically assigned to the interfacial reactions for Li-ion transport at the surface of the LiCoO₂ particles [15]. All the cells with or without additive show an almost identical impedance value at high-frequency range after one cycle or 150 cycles. However, in the mid-frequency range, as shown in Fig. 6(b), Li⁺ migration through the surface film is prompted by the MMDS decomposed products, exhibiting a lower impedance value. This supports the assumption that an ionic conductive film can be formed on the cathode surface in the case of MMDS additive, which is helpful for the intercalation of Li⁺ to the LiCoO₂ particles, and thus improves the cyclic performance of LIBs (Fig. 4).

3.3. Effect of MMDS on the surface composition of LiCoO₂

In order to further understand the source of superior capacity retention of LIBs with 0.5 wt.% MMDS in the electrolyte, the electrode after 150 cycles was analyzed by XPS. The element

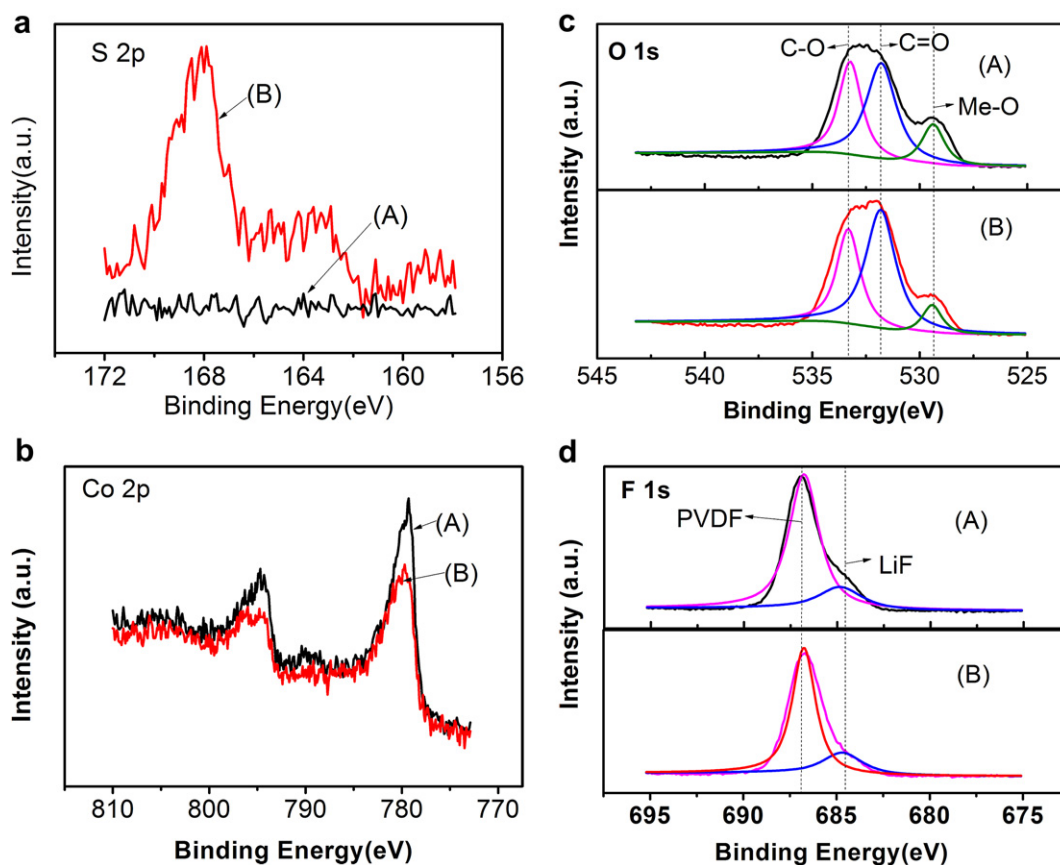


Fig. 7. The S 2p (a), Co 2p (b), O 1s (c) and F 1s (d) XPS spectra of the cycled cathode (A) without additive and (B) with MMDS in the electrolyte.

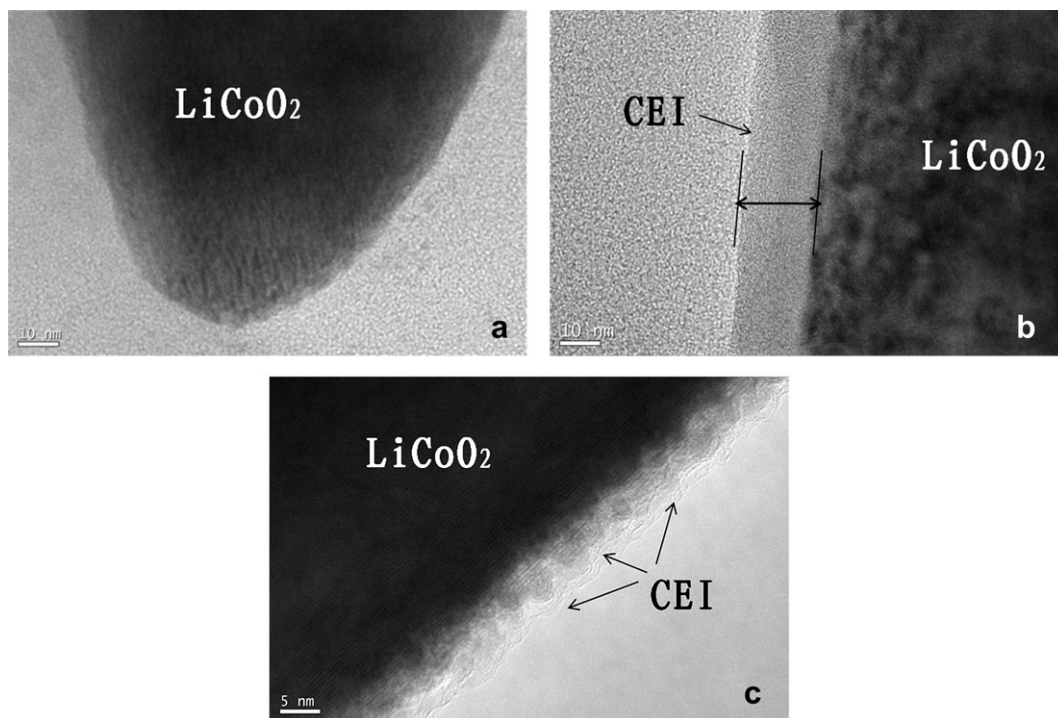


Fig. 8. TEM images of LiCoO₂ electrode: (a) fresh, (b) without MMDS after 150 cycles, and (c) With MMDS after 150 cycles.

concentrations of surface layer are summarized in Table 1, and the S 2p, Co 2p, O 1s and F 1s XPS spectra of the cycled cathode with and without MMDS are shown in Fig. 7.

From the data presented in Table 1, it can be seen that the concentration of C in the cathode cycled in the electrolyte with MMDS is decreased, which means more inorganic degradation products formed on the surface rather than oxidation of solvents in the electrolyte.

Owing to all the cathodes were prepared with a PVDF binder, the peaks associated with PVDF (C 1s, 290.3 eV and 285.7 eV) are similar with the peaks of polyethylene carbonate (PEC) (C1s, 289.0 eV and 286.4 eV), not too much difference can be observed whether the cathode is cycled in the electrolyte without or with 0.5% MMDS, hence the C 1s spectra are not shown here [16]. Compared to the cathode extracted from the cell cycled without additive, additional peaks characteristic of S (2p, 168 eV) are presented on the cathode extracted from the cell cycled with MMDS in the electrolyte, indicating that its surface is covered by a layer originating from MMDS. The Co 2p spectrum is split into two parts due to spin-orbit coupling Co 2p_{3/2} and Co 2p_{1/2} [17]. The cathodes with MMDS have a lower amount of Co content than that of the cathode without additive, which is also consistent with a thin layer formed on the cathode surface.

Differences are observed in O1s spectra with or without MMDS. The peaks of cathode surface without additive is mainly composed of Me-O (1s, 529.5 eV), C=O (1s, 531.5 eV) and C-O (1s, 533.5 eV), which is consistent with the presence of metal oxide (1s, 529.5 eV), Li₂CO₃ (531.5 eV), and PEC which is the polymerization of EC solvent at high potential [9,16]. With addition of MMDS in the electrolyte, the relative intensity of the C-O decreases and C=O increases, which means the MMDS can hinder the polymerization of EC solvent efficiently.

The F1s peak at 687.7 eV corresponds to the C-F bond in the PVDF binder and the peak at 684.5 eV is assigned to be LiF [18]. The peak of LiF (684.5 eV) of the LiCoO₂ electrode cycled with MMDS in the electrolyte shows slightly lower intensity than that of without

additive, which means less compact and resistive substance is formed on the electrode surface [19,20]. The improved battery performance using MMDS as additive in the electrolyte can be ascribed to the higher ionic film formed on the LiCoO₂ surface with lower content of LiF, which promotes charge transport at the electrode active particles/liquid electrolyte interface, and consequently improves the capacity cycle during following cycles at higher voltage.

3.4. Effect of MMDS on the surface morphology of LiCoO₂ electrode

To further investigate the effect of the MMDS on the LiCoO₂ electrode, Transmission electron microscopy (TEM) of electrodes was also examined before and after the cycling test. Fig. 8 shows the TEM images of a fresh LiCoO₂ electrode before the exposure to electrolyte and the electrodes after 150 cycles with or without additive. Compared to the fresh cathode (Fig. 8(a)), it can be found that both the surface of cycled electrodes show significant change (Fig. 8(b–c)). There are some substances covered onto the surface of the cathode, which produced from electrolyte decomposition, forming thick residue film. From Fig. 8(b–c), it is evident that the surface layer derived from MMDS has a thickness approximately 3–5 nm. The film is thinner than that derived from the electrolyte without additive, which reveals a thickness about 15–20 nm. This thinner surface film would decrease the interfacial resistance of the cell, and result in improving the performance of the lithium ion cell.

4. Conclusions

MMDS is firstly evaluated as an electrolyte additive for the formation of a good cathode layer on the LiCoO₂ electrode at high voltage (4.5 V). Addition of 0.5 wt.% MMDS in the electrolyte can significantly improve the cyclic performance of LiCoO₂/graphite cells. After 150 cycles, the discharge capacity retention increased from 32.0% to 69.6%. This is ascribed to the modification of components of cathodes surface layer in the presence of MMDS.

The mechanism of the enhancement of interface layers has been investigated by LSV, CV, EIS, XPS and TEM. It was found that MMDS seems to be preferentially oxidized to form a cathode electrolyte interface layer, and can prevent carbonate solvents from further oxidation continuously. The modified surface possesses highly ionic conductivity and hence improves the LiCoO_2 cathode performance during high voltage operation up to 4.5 V.

Acknowledgements

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